

Advance polymeric membrane to CO₂ separation

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ABSTRACT

Global CO₂ emissions have increased steadily due to use of fossil fuels and industrial applications. Therefore, it is necessary to decrease of energy consumption and CO₂ concentration by CO₂ separation from natural gas. There are different technologies to CO₂ separation. CO₂ separation membranes prepared by green, simple, and efficient methods have faced great challenges. In recent years, Polymer based membrane materials be applied in vast variety of the membrane materials. Polymeric membrane materials show high permeability to CO₂. But having excellent selectivity should be considering preparing polymeric membranes. This review summarizes advances in polymeric materials having very high CO₂ permeability and excellent CO₂/N₂ selectivity that enhance the performance of polymeric membranes. Five important classes of polymer membrane materials are highlighted: polyimides, thermally rearranged polymers (TRs), substituted polyacetylenes, polymers with intrinsic microporosity (PIM) and poly (ethylene oxide) (PEO) that are high performance to CO₂ separation.

Keywords: polymeric membrane; CO₂ separation; gas transport properties; gas separation membrane.

1. Introduction

The increasing of CO₂ emission in world due to industrial activities is great problem to developed country and developing country. The level of CO₂ emission due to fossil fuel combustion and other industrial activities was 37Gt CO₂ in 2014. According to the National Oceanic and Atmospheric Administration (NOAA), USA, the concentration of CO₂ at atmosphere show the level of CO₂ reach 400ppm in 2015 that the highest level of concentration. It be predicted the level of CO₂ in atmosphere have had increasing trend [1].

There are lots of methods to CO₂ separation. CO₂ separation technologies are Cryogenic distillation, absorption, adsorption and membrane separations. The selection of this methods has related to operation condition such as temperature, pressure, concentration. Also it depends on desirable purity CO₂, cost, reliability. etc. despite of high efficiency Cryogenic distillation method in CO₂ separation, the operating of temperature is very low [2].

Also, Physical and chemical absorption are favourable method to CO₂ separation but applying these methods need to recovery absorbent after separation operation. Therefore, absorption technology need to high cost and high energy. And the other hand, about all technologies should be considered the problems of environmental impacts. Recently, Membrane technology has attracted to CO₂ separation from gas mixture. membrane technology is favorable method reasons of intrinsic advantages such as high energy, high efficiency, operation simplicity and reliability, module compactness and modularity. Membrane technology do not occur changing in phase and need to low maintenance. Also, membrane technology has high flexibility in scale up and can be run in areas that have some benefits [1].

The importance of problems about membrane technology is the selection of material. In fact, the type of material is the core of membrane preparing. Generally, membranes classified three type bases on material that be used in membrane preparing: polymeric, inorganic and

polymer-inorganic hybrid. Polymeric membrane has high efficiency, excellent mechanical properties, and high process ability for gas separations. Polymeric membranes be used to CO₂ gas separation During the past decades [3].

In general, to high performance of separation operating is required high permeability and high selectivity for a specific species in a mixture. Glassy or rubbery polymers show an empirical relationship between permeability (P) and selectivity in gas mixtures. Membranes that have high permeability show low selectivity. Upper bound Robeson shows relationship between permeability and selectivity in 1991.

Also with new polymeric material be modified in 2008. There are lots of materials that have been investigated for gas separation membranes but a few polymeric membranes have process ability in industrial application [4].

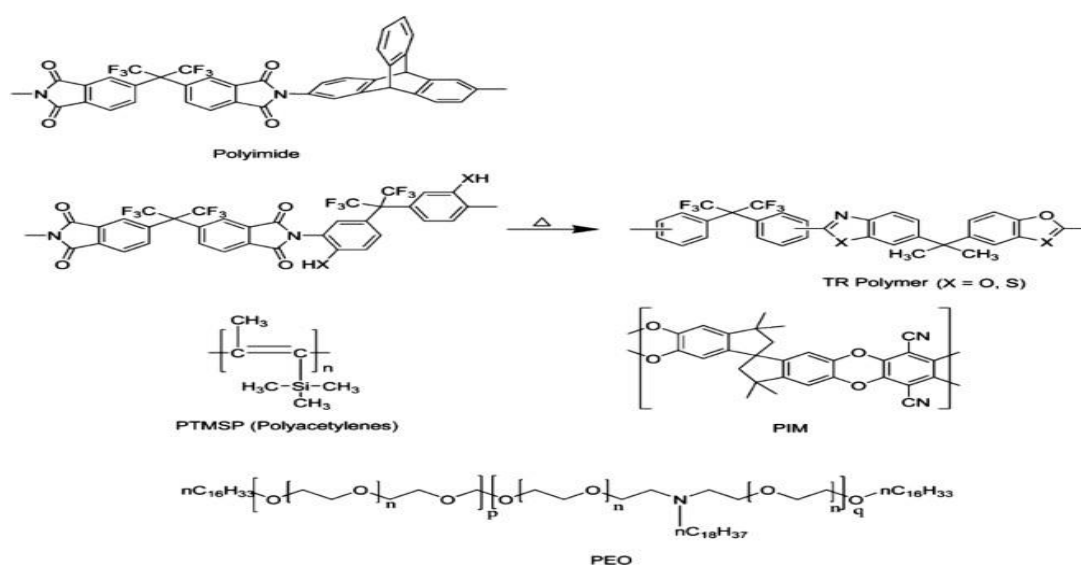


Fig 1. Representative chemical structure of polymer with highCO₂ permeability [3].

General principles of membrane gas separation

The gas transport membrane be explained with permeability and selectivity and the separation performance investigated with two parameter addition to solubility. Permeability be defined as the flux that across from, diffusivity is as known mobility of the molecules within the membrane and solubility is the solubility of gas molecules into membrane.

membrane The relationship for permeability, selectivity and solubility be followed by equation [3]: that P is the permeability coefficient ($\text{cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$), D is diffusivity coefficient ($\text{cm}^2 \text{ s}^{-1}$) and S is the solubility coefficient ($\text{cm}^3 \text{ (STP) cmHg}^{-1}$). The common measurement of P is the barrer ($10^{-10} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$). P permeability is an index to determine separation performance. Addition of barrer the unit of GPU can be used to gas transport membrane. The unit of GPU is $10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.

There are experimental relationships to determined solubility but commonly it is determined experimental dates. The solubility coefficient depends on the type of material that be applied within membrane.

Generally, membranes base on polymer be derived to rubbery and glassy polymers that depends on glass transition temperature. There is low gas-polymer interaction for permeable gases, especially glassy polymer and the gases with little diameter have more diffusion via membrane.

Therefore, improvement of gas separation membrane should be considering by two type of polymer and the choice of the type of polymer is important [2, 3].

In this review be tried to describe polymeric membrane that have high efficiency to CO₂ separation and be highlighted high efficiency polymers that be use to gas separation membrane such as: polyimides, thermally rearranged polymers (TR polymers), substituted polyacetylenes, polymers of intrinsic microporosity (PIM), (ethylene oxide) (PEO)-based polymers (Fig 1).

Polyimides

Polyamides (PAs) are amorphous polymers that have special chemical resistance, high mechanical strength, good thermal stability [5, 6]. These polymers are as primary material to produce polyimides. Among glassy polymers, aromatic polyimides (PIs) are appealing materials for gas separation owing to their excellent gas permeability and selectivity and also

good physico- chemical properties [3, 7, 8] other applications of aromatic polyimides (specially polyamide and polyimides contain of oxiazole are good selection to electronic application [9]) are microelectronics and photoelectronics industries as alignment films in displays, circuit boards, photoresists and dielectric films [8]. polyimides are produced by condensation reaction of an aromatic amine and an aromatic anhydride group (Poly ethylene oxide (PEO) Ordinary, poly ethylene oxide (PEO) base membranes apply to separation of CO₂ because of high affinity for acidic gases and organic vapors. PEOs have high performance and easy fabrication due to drastic interaction polar ether oxygen atoms and CO₂. Permeability of H₂, N₂, and O₂ gases don't change by increasing of end of polar ether oxygen. But oxygen atoms case be crystallite and high chain packing that lead to decrease gas permeability. Pure PEOs usually don't use for gas separation. Some strategy proposes to reduce of crystallization. In fact, molecular weight and content of ethylene oxide or regulation of micron- domain morphology able for reduction of crystallization in PEO. For example, preparing of purely PEO polymers with highly amorphous can be help it. Some purely PEO structure is block copolymer with short ethylene oxide segment that case be reduction of crystallization in temperature room, and enhancing of branch with bulky group, cross-links are most attractive such as using of DME end group of PEG decrease PEO crystallization and increase separation by micro-phase separation [3, 13-15]. This polymer has properties like reverse-selective membrane [10]. Copolymers have structure of micro phase-separate including of soft PEO segments and hard segments such as polyamides (Pebax, polyether block amide for different application such as wire coating and textile fibers), polysulfons and nanocomposite, Hard segment lead to increase of mechanical stability and obstruct crystallization in PEO that case be application it in the actual practical [3, 14, 15]. Also, Multi block copolymer contain of PEO be used to separation CO₂. Such as

Poly (ethylene oxide- b-amide), Pebax (producing from various poly(ether- amide). Studying of these copolymers is limit because of some problem in solubility.

Therefore, new multi block copolymers be investigated such as poly (ethylene oxide)-(butylene terephthalate)

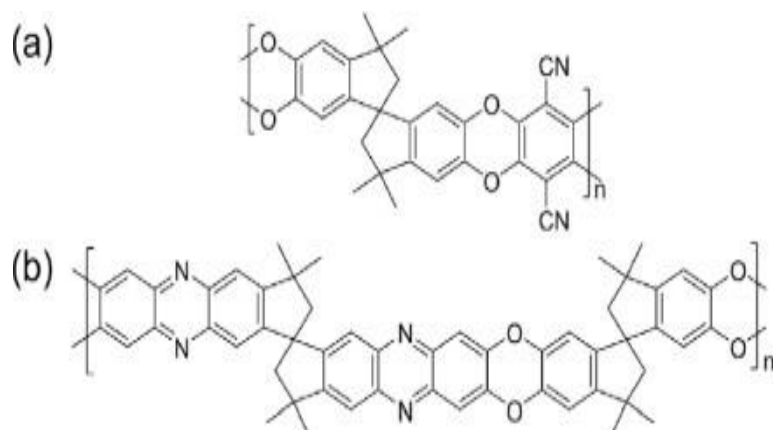


Fig. 2. Complete mechanism for thermal rearrangement of hydroxyl-polyimide to polybenzoxazole [11].

with Commercial name Polyactive. However, there are solubility problems. Crystallization of the structure polymer in the hard phase increase separation performance due to inducing of flexible segments inter-dispersed). One of the main characteristics of PIs as compared to PAs is their higher thermal stability [5]. Also low solubility aramids is result of their rigid backbones and strong interchain interactions therefore polyamides have problems in processing [10]. Polyimide membranes are suitable to separate aromatics from aromatic and aliphatic mixtures because of high affinity polar imide functional groups with electrons of aromatic rings. Another special trait of polyimides is the intra and interchain charge transfer complex (CTC).

Aromatic polyimides have low solubility, however, there are some method to increase solubility such as incorporating of ester, amide or other flexible and pendant group. These methods induce CTC, chain packing and electronic polarization interaction [11].

A few commercial polyimides are soluble such as Ultem, P84 and Matrimid These polyimides have high selectivity and low permeability [12]. Intrinsically, polyimides and

polyimides have high potential to create interchain hydrogen bonding because of high resistance toward aggressive feeds containing condensable components [13].

Thermally rearrangement polymer (TR)

As be known, high performance of membrane is in means of high permeability and selectivity. Heat treatment is another method to increase performance of membrane. The size of voids in polymeric membranes create porosity. Thermal post-membrane conversion can be used to lead to uniform size of voids that is known to rearranged (TR) process. Park et al. synthesized TR polymers that be used to CO₂/CH₄ separation [14]. High free volume in TR membrane related to micropore that case be increase permeability while selectivity is stable due to rigid-rod benzoxazole structure [15]

Hence, connecting of voids morphology is good in tailored free volume. TR membrane have high permeability and selectivity for gas molecules and ions [3]. Depend on ortho position can be forms of polybenzimidazoles, polybenzothiazoles, and polybenzoxazoles[11]. The random chain conformation is one of the reasons tuning size cavity. Dense polybenzoxazole (PBO) and polybenzothiazole (PBT) membranes be produced from thermally rearrangement polyimides cantaning of –SH, –OH ortho functional groups [3]. Ordinary, Polybenzoxazoles be applied to prepare TR membranes due to insolubility in organic solvents and high resistance to chemical environment [12]. TR mebranes show high selectivity for CO₂/CH₄ separation. [3]. PBO be produced from thermally rearrangement aromatic polyimides and ortho- hydroxyl group and N-C bound. Ordinary, thermally rearrangement be done under 300-500°. Complete mechanism be shown in Figure 2 [14].

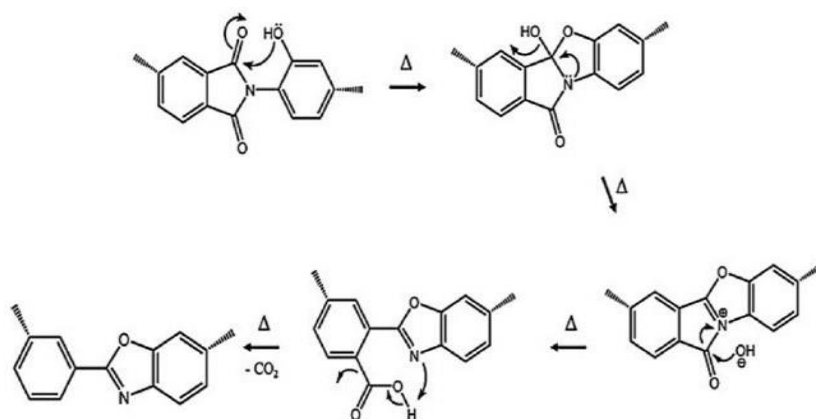


Fig. 3. reaction of amine with anhydride to form an imide[5].

Poly ethylene oxide (PEO)

Ordinary, poly ethylene oxide (PEO) base membranes apply to separation of CO₂ because of high affinity for acidic gases and organic vapors. PEOs have high performance and easy fabrication due to drastic interaction polar ether oxygen atoms and CO₂. Permeability of H₂, N₂, and O₂ gases don't change by increasing of end of polar ether oxygen. But oxygen atoms case be crystallite and high chain packing that lead to decrease gas permeability. Pure PEOs usually don't use for gas separation. Some strategy proposes to reduce of crystallization. In fact, molecular weight and content of ethylene oxide or regulation of micron- domain morphology able for reduction of crystallization in PEO. For example, preparing of purely PEO polymers with highly amorphous can be help it. Some purely PEO structure is block copolymer with short ethylene oxide segment that case be reduction of crystallization in temperature room, and enhancing of branch with bulky group, cross-links are most attractive such as using of DME end group of PEG decrease PEO crystallization and increase separation by micro-phase separation [3, 13-15]. This polymer has properties like reverse-selective membrane [12]. Copolymers have structure of micro phase-separate including of soft PEO segments and hard segments such as polyamides (Pebax, polyether block amide for different application such as wire coating and textile fibers), polysulfons and nanocomposite, Hard segment lead to increase of mechanical stability and obstruct crystallization in PEO that

case be application it in the actual practical [3, 14, 15]. Also, Multi block copolymer contain of PEO be used to separation CO_2 . Such as Poly (ethylene oxide- b-amide), Pebax (producing from various poly(ether- amide)s). Studying of these copolymers is limit because of some problem in solubility. Therefore, new multi block copolymers be investigated such as poly (ethylene oxide)- (butylene terephthalate) with Commercial name Polyactive. Howbeit, there are solubility problems. Crystallization of the structurepolymer in the hard phase increase separation performance due to inducing of flexible segments inter-dispersed between the rigid segments, PEO, PDMS and a rigid segment in the tri-block copolymers increase solubility, permeability, the mechanical and thermal stability, similar to di-block copolymer including of PEO and PDMS [13]. PEO phase in these copolymers increase diffusivity due to continuous pathway.

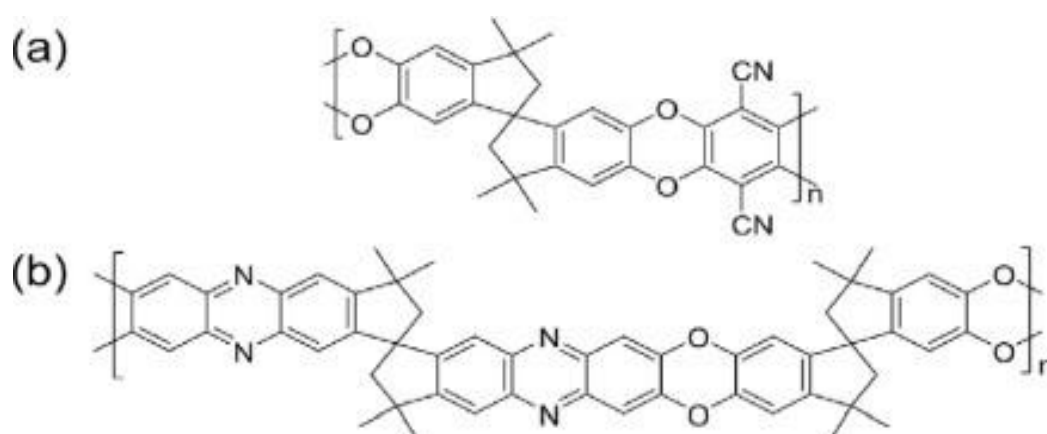


Fig. 4. Complete mechanism for thermal rearrangement of hydroxyl-polyimide to polybenzoxazole [14].

Morphology by domain shape and spatial arrangement due to the hard segment composition and the lengths of the PEO and hard segment blocks effect on gas permeability (figure 4) [3, 15] Copolyimides containing of ethylene oxide comparing to pure polyimides have higher diffusivity for CO_2 , N_2 gases. The mobility of chain decrease due to glassy polyimides. Also polyimides enhance mechanical properties of copolyimides. So Mico-phase in PEO contribute in gas diffusion and micro-domain in polyimide improve mechanical strength. As shown in figure 15 with increasing of PEO molecular weight induce diffusivity and

permeability. PEO- polyurethane be used for biomedical and gas separation applications due to high mechanical properties and structural interchangeability. Other rubbery material with PEO can be used in copolymers such as poly(propylene oxide) , PDMS, siloxanes, and dendrimers [15].

Substituted polyacetylenes

these polymers be produced from bulky pendant groups and be prepared from polymerization acetylenic monomers. The pendant groups obstruct of rotation membrane backbone. These polymers have large free volume fraction. Hence, they show high permeability. cis-rich poly(1-trimethylsilyl-1-propyne) (PTMSP) and polymers in this class often have high permeability for any gases. In spite of high permeability show low selectivity according to Robeson upper bound limit. And the other hand, if polyacetylene-based membranes will be applied to CO₂ separation, they will be show strong physical aging. Nevertheless, some methods be applied to modification of structure polymer such as cross-linking and grafting [3].

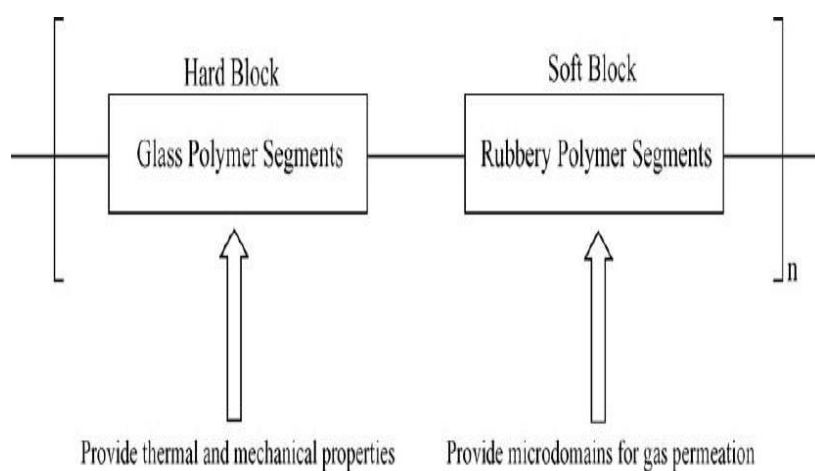


Fig. 5. Synthetic strategy for polymer structure used as CO₂ separation membrane [1].

Polymers intrinsic microporosity (PIM)

PIMs are new class of polymer that show high permeability, selectivity and firstly be introduced by Budd and McKeown research groups. PIMs have high solubility in common

solvents. Most PIMs that be used to preparing embrane are PIM-1 and PIM-2 (figure 5) Usually, poly(trimethyl-silyl-propyne) (PTMSP) be compared with PIM-1 [18]. Generally, PIMs be produced from polycondensation reaction of tetrahydroxy-monomers containing spiro- or contorted centres with tetrafluoromonomers. PIMs are including of pores with the diameter of less 2 nm [3].

Conclusions

Membrane technology has important role to CO₂ separation and improvement performance of polymeric membrane can be helped it. thus, the choice of suitable material to gas separation membrane is key parameter to enhance of gas transport properties that have high permeability and excellent selectivity. Polyimides, TR polymers, poly(ethylene oxide)s, substituted polyacetylenes and PIMs have high potential to improve polymeric membrane.

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